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KOKAI TOKKYO KOHO

1. Title of the Invention

METHOD FOR MANUFACTURE OF  
ULTRATHIN COPPER FOIL

2. Inventor: Masanobu Yokoyama

c/o Furukawa Electric Co., Ltd., Nikko  
Research Laboratory  
500 Kiyotaki-machi, Nikko-shi, Tochigi  
Prefecture

(and one more inventor)

3. Patent Applicant

(529) Furukawa Electric Co., Ltd.  
2-6-1, Marunouchi, Chiyoda-ku, Tokyo  
Representative and Representative Director:  
Masao Funabashi

(and one more applicant)

4. Patent Representative: Patent Attorney: (5847)  
Takehiko Suzue (and one more party)

Address:  
No. 17, Mori Building  
2 Sakuragawa-cho, Shiba Nishikubo  
Minato-ku, Tokyo 105  
Telephone: 03 (502) 3181 (main line)

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Specification

1. Title of the Invention

METHOD FOR MANUFACTURE OF ULTRATHIN COPPER FOIL

2. Patent Claims

A method for the manufacture of an ultrathin copper foil by conducting zinc substitution plating on the edge portion of one surface of an aluminum foil or aluminum alloy foil, then conducting copper plating to a thickness of 0.5-12 µm in a copper pyrophosphate plating bath on

the entire surface of said surface, and then conducting copper plating to a thickness of 8-12  $\mu\text{m}$  in a copper sulfate-based copper plating bath on the outside thereof.

### 3. Detailed Description of the Invention

The present invention relates to a method for the manufacture of an ultrathin copper foil for high-density printed circuit boards in which a wiring width and wire spacing are greatly decreased.

In recent years, significant progress in electronics technology created a demand for highly reliable high-density printed circuit boards. In particular, in the copper-clad laminates for printed circuits of computers, it became necessary to form ultrafine circuits with a wiring width and wiring spacing of no more than 0.2 mm. However, the thickness of the conventionally used copper foils was as large as about 85  $\mu\text{m}$ . Therefore, in the etching technology at the time, when circuits were formed from such copper foil-clad laminates, there was a danger that the copper foils would be undercut by side etching (a lower side portion of a groove is etched on the periphery thereof and a recess-like portion is obtained), causing a short circuit. For this reason, circuits with high-density wiring widths and wiring spacing could not be obtained. Therefore, it was impossible to obtain highly reliable printed circuits with a high density.

Accordingly, thin copper foils with a thickness of 18-25  $\mu\text{m}$  were used to attain this object. However, since they were manufactured by electrolytic methods similar to those for the manufacture of the above-mentioned thick copper foils, pinholes easily occurred. Moreover, because the foils were so thin, "wrinkles" and "scratches" could easily occur when the foils were handled. A low production yield and a high cost were other drawbacks associated with such ultrathin foils. Furthermore, when such copper foils were employed for forming high-density circuits by a photoresist method, the lower limit for the wiring width and wiring spacing was 0.2 mm, and high-density circuits with an ultrafine pattern having wiring widths and spacing less than this limit were difficult to produce.

An improved method was suggested, this method using an ultrathin copper foil formed by employing an aluminum foil, etc. as a pseudo-substrate and electroplating a copper layer with a thickness of no more than 18  $\mu\text{m}$  thereupon. A glass-epoxy base material was laminated on the copper foil surface, the aluminum foil serving as a pseudo-substrate was removed by chemical or mechanical peeling method, and the resulting copper foil laminated sheet was used to form a high-density circuit by the aforesaid photoresist process. Such a method is disclosed, for example, in Japanese Patent Application Laid-open 48-85857.

However, with such a method, it is necessary to conduct zinc substitution plating on the electrocoating surface of the aluminum foil in advance in order to provide for good bonding strength of the ultrathin copper layer formed by electroplating with the aluminum foil serving as a pseudo-substrate and it was also necessary to dissolve and remove the aluminum and zinc chemically in order to obtain a copper clad laminate after lamination of the glass-epoxy base material. Therefore, in addition to those two types being complicated and wastewater treatment being difficult, there are disadvantages in that the copper layer is partially dissolved when the zinc is removed, and circuit shorts occur easily.

With another suggested method, copper cyanide plating is conducted on one surface of the aluminum foil of the pre-degreased and activated pseudo-substrate. However, in such a case, the copper adhesion strength is insufficient. For this reason, when in subsequent processes a thick copper plating was conducted with an acidic copper plating bath and then treatment was

conducted to increase the adhesive force, the copper layer could be easily peeled off and removed from the surface of aluminum foil. Moreover, when the thickness of the copper plating was less than 12  $\mu\text{m}$ , a large number of fine pinholes were present and the product was not suitable for practical use.

The inventors have conducted an intensive study aimed at the resolution of the above-described problems. Based on the results obtained, a method was developed for the manufacture of an ultrathin copper foil designed for the formation of highly reliable printed circuits with a high density. Thus, with the method in accordance with the present invention zinc substitution plating is conducted on the edge portion on one surface of an aluminum or aluminum alloy foil (referred to simply as aluminum foil hereinbelow), then copper plating is conducted to a thickness of 0.5-12  $\mu\text{m}$  in a copper pyrophosphate plating bath on the entirety of that one surface, and then copper plating is conducted to a thickness of 8-12  $\mu\text{m}$  in a copper sulfate-based copper plating bath on the outside thereof.

The method in accordance with the present invention will be described hereinbelow in greater detail.

At least one surface of an aluminum foil with a thickness of 30-70  $\mu\text{m}$  (a long foil with a width of 300-1300 mm) is degreased with an alkaline cleaner and washed with water according to the usual procedure. If necessary, washing with water is conducted after pickling with 50%  $\text{HNO}_3$  or activation.

Then an edge portion on one surface of the foil is immersed for 2-120 sec in the so-called zincate bath and zinc substitution plating is conducted. In this case, the edge portion as referred to hereinabove is a frame-like portion located on the periphery of the aluminum foil; it has a width of 2-100 mm, preferably, 10-50 mm. This width is referred to as an edge width.

The zinc substitution plating is conducted to improve adhesion of copper layer to the aluminum foil in the portions that are directly subjected to copper plating. Thus, when the end portion of the aluminum foil is not subjected to zinc substitution plating, a copper pyrophosphate plating itself cannot provide for a sufficient bonding strength with the surface of aluminum foil. When, in such a state, water washing and copper sulfate thick plating are performed in the subsequent process, the copper layer can easily peel from the edge portion of the aluminum foil. Moreover, if the coating peels off even slightly, then water or plating solution rapidly penetrates into the interface between the aluminum foil and copper layer, the surface of aluminum foil is corroded mainly by the plating solution, and the peeling is further promoted. Even if the substrates in such a state are finally dried, since the major portion of the copper layer has peeled from the pseudo-substrate, "wrinkles" or a large number of pinholes appear therein, making the foil unsuitable for practical use. However, if zinc substitution plating of the edge portion of aluminum foil is conducted as described above, the bonding strength with respect to the copper pyrophosphate plating bath is also improved and no peeling occurs in subsequent plating in a copper sulfate bath. Moreover, when the copper plating is formed to a thickness of no less than 5  $\mu\text{m}$ , practically no pinholes are formed.

Immediately after completion of the zinc substitution plating, a copper layer with a thickness of 0.5-12  $\mu\text{m}$  is plated by using a copper pyrophosphate plating bath, followed by washing with water. In such a case, no specific limitation is placed on the composition of the copper pyrophosphate plating bath, but it is preferred that the copper concentration be 5-100 g/L, the concentration of potassium pyrophosphate be 100-500 g/L, and the pH be 8-12. As for the plating conditions, the bath temperature is within a range from normal temperature to 70°C, the electric current density is 1-5 A/dm<sup>2</sup>, and the electrolysis time is 5-25 sec.

The copper pyrophosphate plating bath is selected for the purposes of the present invention because the coating obtained with such a bath has better adhesion to aluminum foils than that obtained with other copper plating baths, and, naturally, no peeling occurs in the lamination of laminated base materials for printed circuits. Furthermore, in addition to that fact that stronger adhesion cannot be maintained, it is not necessary to chemically dissolve and remove the aluminum foil pseudo-substrate after lamination of the base material, and peeling can be conducted by a simple mechanical means. As a result, wastewater treatment is made unnecessary, and the aluminum used can be easily recovered in the form of aluminum chips. Furthermore, a copper pyrophosphate plating bath makes it possible to conduct uniform electrocoating, and a coating can be obtained which is smooth and has good gloss. Moreover, a very small number of pinholes appear even when a thin copper foil is obtained. The thickness of the copper pyrophosphate plating is limited to 0.5-1.2  $\mu\text{m}$  for the following reasons. When the thickness is less than 0.5  $\mu\text{m}$ , the number of pinholes in a thin copper foil obtained increases, making it unsuitable for practical use. On the other hand, when the thickness exceeds 12  $\mu\text{m}$ , since the upper limit of thickness of thin copper foils is 15  $\mu\text{m}$ , the copper sulfate plating in the subsequent process cannot be conducted. Moreover, adhesion to plastic laminated base materials is degraded. The thickness of the copper foil layer is preferably 2-7  $\mu\text{m}$ .

Plating copper to a thickness of 8-12  $\mu\text{m}$  in a copper plating bath containing copper sulfate is conducted as a method for roughening of the copper foil layer. Appropriate conditions of such treatment should be selected and no specific limitation is placed thereon. Typically the copper plating bath has a copper concentration of 20-60 g/L and a sulfuric acid concentration of 40-150 g/L. The bath temperature is preferably within a range from normal temperature to 60°C. As for the electric current density and electrolysis time, they are somewhat affected on the liquid flow parameters, stirring state, and plating thickness, but preferably they are usually within the ranges of 5-40 A/dm<sup>2</sup> and 1-10 min, respectively. The external appearance of the obtained copper plated film must be such that velvety peaks and valleys of red color are formed.

The thickness of the copper plated layer is limited to 8-12  $\mu\text{m}$  for the reasons as follows. The entire thickness of plated copper layer may be 15  $\mu\text{m}$  and the thickness of the plated layer obtained by using a copper sulfate bath may be adjusted by varying the thickness of the plated layer obtained with the above-mentioned copper pyrophosphate plating bath.

The plated layer with the above-mentioned roughening treatment is further laminated with a plurality of layers of a composition prepared by infiltrating an insulating substance such as glass fibers with an epoxy resin, and then the aluminum foil pseudo-substrate is peeled off, thereby obtaining a final product.

In this case, the bonding strength between the plated copper layer subjected to the roughening treatment and said laminated insulating material may be about 1.6-1.8 kg/cm<sup>2</sup>, but if it is less than 1.6 kg/cm<sup>2</sup>, secondary roughening treatment copper plating is conducted on the outer side of the copper plated layer. For this purpose a method can be used in which, for example, cathodization is conducted at a current density of 2-20 A/dm<sup>2</sup> for 2-120 seconds in an acidic copper electrolytic bath having added therein ions of at least one metal selected from a group including arsenic, antimony, and bismuth.

Embodiments of the present invention will be described hereinbelow

### Embodiment 1

A soft pure aluminum foil (99.9%) with a thickness of 70 µm was degreased by immersion for 3 min in a solution of sodium orthosilicate (100 g/L) at a temperature of 70°C, and then pickling and activation treatment was conducted by immersion for 1 min at a temperature of 25°C in an aqueous solution of HNO<sub>3</sub> with a concentration of 350 g/L. Then, an edge portion (edge width 20 mm) on only one side of the aluminum foil was selectively subjected to local zinc substitution plating by immersion for 60 sec in a solution (liquid temperature, room temperature) consisting of ZnO 30 g/L and NaOH 100 g/L. Then, one side of the aluminum foil was plated with copper for 5 min at an electric current density of 2 A/dm<sup>2</sup> in a plating bath (liquid temperature 50°C) having a Cu concentration of 30 g/L and a potassium pyrophosphate concentration of 150 g/L and a pH of 8.8. Finally, the plated layer was subjected to roughening copper plating for 2 min at a current density of 10 A/dm<sup>2</sup> in a plating bath (liquid temperature 20°C) containing Cu at 20 g/L and H<sub>2</sub>SO<sub>4</sub> at 75 g/L. As a result, an ultrathin copper foil with a copper layer thickness of 6 µm was obtained.

### Embodiment 2

A hard aluminum alloy foil (Al 99.7%, Cu 0.05%, Fe 0.05%, Si 0.20%) with a thickness of 30 µm was subjected to degreasing by immersion for 30 sec at a temperature of 50°C in a solution containing sodium orthosilicate 100 g/L, NaOH 30 g/L, and nonionic surfactant 0.1 g/L. Then, pickling and activation treatment was conducted by immersion for 30 sec at a temperature of 25°C in a solution consisting of HCl 100 g/L and NaCl 50 g/L. Then, local zinc substitution plating was conducted selectively only on the edge portion (edge thickness 35 mm) on one side of the aluminum alloy foil by immersion for 38 sec in a solution (liquid temperature, room temperature) consisting of ZnO 5.0 g/L, NaOH 200 g/L, and FeCl<sub>3</sub> 5 g/L. One surface of the aluminum foil was then plated with copper for 10 min at a current density of 3 A/dm<sup>2</sup> in a plating bath (liquid temperature 60°C) consisting of Cu 80 g/L and potassium pyrophosphate 30 g/L, and having a pH of 9.3. Then roughening copper plating of said plating layer was conducted for 60 sec at a current density of 6 A/dm<sup>2</sup> in a plating bath (liquid temperature 25°C) consisting of Cu at 30 g/L and H<sub>2</sub>SO<sub>4</sub> at 100 g/L. Finally, the resulting roughened plated layer was subjected to secondary roughening copper plating for 20 sec at a current density of 6 A/dm<sup>2</sup> in a solution consisting of Cu (BF<sub>4</sub>)<sub>2</sub> 25 g/L, HBF<sub>4</sub> 42 g/L, Na<sub>3</sub>AsO<sub>4</sub>·12H<sub>2</sub>O 0.9 g/L (liquid temperature 12°C), and an ultra thin copper foil with a copper layer thickness of 7 µm was obtained.

### Embodiment 3

A hard aluminum alloy foil (Al 99.3%, Cu 0.04%, Fe 0.07%, Si 0.15%, Zn 0.05%, Mg 0.10%, Ti 0.05%) with a thickness of 50 µm was subjected to anodic electrolytic degreasing for 30 sec at a current density of 2 A/dm<sup>2</sup> in a solution containing sodium orthosilicate 100 g/L, NaOH 30 g/L, and a nonionic surfactant 0.1 g/L. Then only the edge portion (edge width 15 mm) of the Al alloy foil was selectively subjected to local zinc substitution plating by treating for 20 sec in a solution (liquid temperature 30°C) consisting of ZnO 70 g/L and NaOH 400 g/L. Then, one surface of the aluminum foil was plated with copper for 15 minutes at a current density of 3 A/dm<sup>2</sup> in a plating bath (liquid temperature 60°C) having a Cu concentration of 100 g/L, a potassium pyrophosphate concentration of 250 g/L, and a pH of 9.0. Then, the copper plated

layer was subjected to roughening copper plating for 75 sec at a current density of 32 A/dm<sup>2</sup> in a plating bath (liquid temperature 65°C) having a Cu concentration of 50 g/L and an H<sub>2</sub>SO<sub>4</sub> concentration of 50 g/L. Finally, the roughened copper plated layer was subjected to secondary roughening copper plating for 32 sec at an electric current density of 4 A/dm<sup>2</sup> in a solution (liquid temperature 15°C) containing Cu at 7 g/L, H<sub>2</sub>SO<sub>4</sub> at 32 g/L, H<sub>3</sub>AsO<sub>4</sub> at 0.4 g/L, and H<sub>2</sub>SiO<sub>3</sub> at 0.2 g/L, and an ultrathin copper foil with a copper layer thickness of 15 μm was obtained.

#### Comparative Example 1

A hard aluminum alloy foil (Al 99.7%, Cu 0.5%, Fe 0.05%, Si 0.20%) with a thickness of 30 μm was subjected to degreasing by immersion for 3 min in a solution (liquid temperature 70°C) consisting of sodium carbonate 30 g/L and sodium phosphate 50 g/L, and then an edge portion of 15 mm on one surface of the aluminum alloy foil was selectively subjected to zinc substitution plating by immersion for 20 sec in a solution containing ZnO at 70 g/L and NaOH at 400 g/L (liquid temperature 30°C). Then, copper plating was performed on the entirety of one surface of the aluminum alloy foil for 15 minutes at an electric current density of 3 A/dm<sup>2</sup> in a plating bath (liquid temperature 40°C) having a Cu concentration of 100 g/L, a potassium pyrophosphate concentration of 250 g/L, and a pH of 9.0, then the copper plated layer was subjected to roughening copper plating for 75 sec at an electric current density of 32 A/dm<sup>2</sup> in a plating bath (liquid temperature 65°C) having a Cu concentration of 50 g/L and an H<sub>2</sub>SO<sub>4</sub> concentration of 50 g/L. Finally, the roughened copper plated layer was subjected to secondary roughening copper plating for 32 sec at an electric current density of 4 A/dm<sup>2</sup> in a solution (liquid temperature 15°C) containing Cu at 7 g/L, H<sub>2</sub>SO<sub>4</sub> at 32 g/L, H<sub>3</sub>AsO<sub>4</sub> at 0.4 g/L, and H<sub>2</sub>SiO<sub>3</sub> at 0.2 g/L, and an ultrathin copper foil with a copper layer thickness of 5 μm was obtained.

#### Comparative Example 2

An aluminum alloy foil identical to that of Comparative Example 1 was used and degreasing was conducted in the same manner as in Comparative Example 1. Then, copper plating similar to that of Comparative Example 1 was conducted immediately without zinc substitution plating and thereafter roughening copper plating was conducted to obtain an ultrathin copper foil with a copper layer thickness of 5 μm.

The ultrathin copper foils with pseudo-substrates attached thereto, which were obtained in the Embodiments 1-3 and Comparative Examples 1-2 were laminated on base materials infiltrated with glass epoxy and then pressing was conducted for 60 min at a pressure of 25 kg/cm<sup>2</sup> and a heating temperature of 160°C to obtain a laminated sheet with a thickness of 2 mm. Copper-clad laminated sheets were then obtained by mechanically peeling off the pseudo-substrates of aluminum foils, copper pyrophosphate plating was thereafter conducted to increase the thickness of the copper layer to 15 μm, and the bonding strength and pinholes were measured by the usual method. The results are presented in Table 1.

The bonding strength was measured by applying a peeling force in the direction of 90° to a width of 10 mm. The number of pinholes was counted by illuminating the layer from below a dark room and observing the transmitted light.

Table 1.

|                       | Number of pinholes<br>(holes/m <sup>2</sup> ) | Bonding strength<br>(kg/cm <sup>2</sup> ) | External appearance of<br>copper foil |
|-----------------------|---|---|---------------------------------------|
| Embodiment 1          | 2-4   | 1.6-1.7                                   | Fine velvety peaks and<br>valleys     |
| Embodiment 2          | 1-2   | 2.0-2.4                                   | "                                     |
| Embodiment 3          | 0   | 20.-2.4                                   | "                                     |
| Comparative Example 1 | 20-100  | 1.5-1.7                                   | Bulbous peaks and<br>valleys          |
| Comparative Example 2 | Very large number                             | 1.4-1.8                                   | "                                     |

As follows from the table presented above, the ultrathin copper foils obtained by the method in accordance with the present invention have a number of pinholes substantially less than that in the ultrathin foils obtained by the conventional methods and also have excellent bonding strength.

Patent Representative. Patent Attorney: Takehiko Suzue.

#### 5. List of Appended Items

- |                             |                      |
|-----------------------------|----------------------|
| (1) Power of attorney       | 2 copies             |
| (2) Specification           | 1 copy               |
| (3) Drawings                | 1 copy 1 [illegible] |
| (3) (4) Copy of application | 1 copy 3 [illegible] |

#### 6. Inventors, patent applicants, and patent representatives other than listed above

##### (1) Inventor

Mitsuru Sato  
c/o Furukawa Electric Co., Ltd., Nikko Research Laboratory  
500 Kiyotaki-machi, Nikko-shi, Tochigi Prefecture

##### (2) Patent Applicant

Furukawa Metals Co., Ltd.  
2-6-1, Marunouchi, Chiyoda-ku, Tokyo  
K. Shiroyanagi, Representative and Representative Director

##### (3) Patent Representative

Takeo Miki, (5743) Patent Attorney

**Address:**

**No. 17, Mori Building  
2 Sakuragawa-cho, Shiba Nishikubo  
Minato-ku, Tokyo**



2000-2 2000-6

## 特許願(1)

特許局長官 著者高橋洋

## 1. 発明の名称

電線端子の製造方法

## 2. 発明者

日本電気株式会社  
古河電気工業株式会社  
横山正義

## 3. 特許出願人

東京都千代田区丸の内二丁目6番1号  
(529) 古河電気工業株式会社  
代表者代理権限者 横山正義  
(権利主名)

## 4. 代理人

日本電気株式会社  
〒100 古河電気工業株式会社  
16F (529) 代表者 横山正義  
(権利主名)  
50 092507. 制度

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|           | CZ6D 5/10 |

## 明細書

## 1. 発明の名称

電線端子の製造方法

## 3. 発明請求の範囲

アルミニウム又はアルミニウム合金の片側面に被覆層を形成する方法、該層の全表面をビロラン脱脂ノックで0.5～1.2μの削りオフを行い、後にその外側に複数個性別ノック層で0.8～1.2μの削りオフを行うことを特徴とする電線端子の製造方法。

## 3. 材料の特徴と効果

本発明は電線端子に複数個性別ノック層で表面を粗化して表面をプリント用の耐候性塗装の附着力を向上するものである。

近年電子機器の激しい進歩に伴い、プリント基板上においてはあらかじめしてあらわされたもののが要求されており、特に電子部品のプリント回路基板上においては、表面粗度に規制が0.3μ以下の中からある条件を形成しなければならない。然しながら実際使用されている

技術は、その多くが約3.0μの粗さであるため、現在のエンジニア技術においては、その粗さをいかにしては、その粗さをいかに削除せしめるか、粗さがマイクロエンジニアリングよりアンダーコントロールの下側部分が周囲側にエクステンダされ、くぼみ状の凹凸が現れる状態をいう)となる問題である。それがあるため、該層をさらに粗い層の高層層の上に形成することができず、更に粗い層を形成して且つあらわされたプリント基板をうるととてもよいものであつた。

従つてこのようを目指して運営する技術としては、1.0～2.0μを越す粗さが使用されているが、この場合表面の厚肉側面の粗さが主因となり、その粗さはよく、且つ表面のため表面に対して、「しわ」「きず」等が発生しある。又多留を多く、コストとなるという欠点があつた。従つてこのよう表面層をフォトレジスト法により表面粗度を形成せしめる場合の問題は粗さは0.3μが下限といわれ、それ以下の

のパターンを有する高密度日本語の内皮は表面で  
あります。

又この改良方法としてアルミニウム箔等を重  
ねるとし、その上に電気ノック法により接着面  
より以下の時間の熱メッシュを加热せしめた各種  
温度を用意し、既述の高密度ガラスエボキシ基板  
を熱風した後、既述のアルミニウム箔を化学  
的又は物理的に剥離アダヒドリウムで固定し、加热  
温度とし、これを用いたフォトレジスト膜にて  
り高密度内皮を形成せしむる方法が例えば特  
開昭51-25687参照され得る。

然しながらこの方法は既述ノックによらず  
される熱力学的条件のアルミニウム箔とを、  
よく密着せしめるために下記のアルミニウム箔  
の熱力学的条件を満足せしめノックしてよく密着があ  
ると共にガラスエボキシ基板を加热し、熱附  
着化するためには化成的アルミニウムと  
やかとを用時密着しなければならない。又つて  
そのと熱が有効でらう且つ露度の熱取扱能で  
あると実用目的を達成するが一體条件とも密接

され、熱力学的条件を生じるい欠点がある。

又他の方法として手動糊合、高密度化した食糸  
熱メッシュノック法の片側上にソアン化成タフ  
ヤードエクソル熱メッシュを行なうこともあるが、  
この場合の時間条件が十分でないため、その他の  
の工場において、熱力学的ノック法による熱力学  
ノックを行い、既述のアダヒドリウム糊から糊出、脱  
離し易く且つ熱メッシュの大きさが1ミリ以下の  
条件には内皮の形成をピンホールが存続し實用  
上に利し得るものである。

今既述はかかる欠点を改善するため改めて実  
験を行つた結果、結果を以て、一熱力学的アリ  
ント熱メッシュを形成するための、熱力学的熱力学  
法を見出したものである。即ち本実験はアルミ  
ニウム箔又はアルミニウム熱メッシュ（以下単にアル  
ミニウム箔といふ）の片側熱面に高密度熱メ  
ッシュを行つた後、該片側熱面にビロリン酸メ  
ソウ液にて0.5～1ミリの熱ノックを行い、更に  
その外側に熱吸収性糊メッシュ層にて0.5～1ミリ

#### ④熱ノックを行つものである。

本熱力学法について以下詳細に説明する。

3.0～7.0ミクのアルミニウム箔（巾3.00～  
1.80ミクの長尺用）の少くとも片面を常温  
のアルカリクリーナー等により脱脂し水洗する。  
又シビの場合は必要により5.0ミクHNO<sub>3</sub>等で酸洗  
し（は過酸化した後本脱する）。

次いで該面の片面の表面を所定レンジケート  
または2～120秒被覆して、直射日光ノック  
を施す。またこの場合該面とはアルミニウム箔  
の周縁に抜けた部分をいい、その巾は2～  
1.0ミク、壁をしくば1.0～3.0ミクである。こ  
の面を最終面といふ。

而して直射日光ノックを施す理由は直射日光ノ  
ックされる部分のアルミニウム箔に対する熱能  
の密着性を向上せしめるためである。即ちアル  
ミニウム箔の表面に直射日光ノックを施せばい  
場合はビロリン酸メッシュ自体アルミニウム  
箔面に対して十分な密着性を保持し得ないため  
であり、このような表面において本脱には最

工場における熱力学的糊メッシュを下記に、  
アルミニウム箔の熱面から糊出が発生するのみ  
ならず且つても糊出すると急速に水又はノ  
ック液がアルミニウム箔と糊との界面に接触  
し、熱メッシュ化により主としてアルミニウム  
の熱面を熱食しつつ一時糊脱を実現する。この  
よう本脱のものを熱力学的糊脱するとして  
も側面の大半が糊脱から離脱しているため  
「しか」又大は熱力学的糊脱を生じる間に  
離せないものとなる。しかし前記の如くアル  
ミニウム箔の熱面直射日光ノックを施すこと  
によりビロリン酸メッシュ層に及ぶ熱能性も及  
びてより且つその他の熱力学的糊脱メッシュ層中  
における熱脱も少くならないと甚だ多く以上の熱ノ  
ックを施せしめた場合ビンホールは数んど見  
られないものとなる。

而して要の熱脱メッシュを施した熱面にビ  
ロリン酸メッシュ層にヨリ0.5～1ミリの熱ノ  
ックを行ひ本脱する。この場合ビロリン酸メ  
ッシュ層の熱能については特に規定するものではな

Cu 0.0 9 g, P 0.0 0 5 g, Si 0.2 0 g) をオルトケイ酸ナトリウム 1 0 0 g/4, NaOH 3 0 g/4, ノーチン不界面活性剤 0.1 g/4 からなる电解液中に 5 0 ℃ において 3 0 秒浸漬して脱脂を行い、次いで HCl 1 0 0 g/4, NaCl 5 0 g/4 からなる电解液中に 3 5 ℃ において 3 0 秒浸漬して脱脂並に活性化処理を行つた後、脱アルミニウム合金箔の片面銀層（銀幅巾 3 5 mm）のみを選択的に Zn 0.5 0 g/4, NaOH 2 0 0 g/4, PdCl<sub>2</sub> 5 g/4 からなる电解液（液温、液量）中に 3 0 秒間脱酸せしめ両分层銀電極メッシュを行つた後、次いで脱アルミニウム箔の片面を Cu 8 0 g/4, ピロリン酸カリウム 3 0 g/4, NH 9.3 からなるメッシュ（液温 6 0 ℃）中にかいて 1 0 分間、電流密度 3 A/cm<sup>2</sup> により鍍メッキを行ひ、次いで脱アルミニウム箔を Cu 酸度 3 0 g/4, H<sub>2</sub>SO<sub>4</sub> 1 0 0 g/4 からなるメッシュ（液温 2 8 ℃）中にかいて 3 0 秒間、電流密度 6 A/cm<sup>2</sup> により凹凸化鋼メッシュを行ひ、次いで脱アルミニウム箔の片面を Cu 酸度 1 0 0 g/4, ピロリン酸カリウム 2 5 g/4, NH 9.0 からなるメッシュ（液温 6 0 ℃）中にかいて 1 5 分間、電流密度 3 A/cm<sup>2</sup> にて鍍メッシュを行ひ、次いで脱鋼メッシュ用

を Cu 酸度 5 0 g/4, H<sub>2</sub>SO<sub>4</sub> 5 0 g/4 からなるメッシュ（液温 6 5 ℃）中にかいて 7 5 秒間、電流密度 3 2 A/cm<sup>2</sup> にて凹凸化鋼メッシュを行ひ、最後に脱凹凸化鋼メッシュの上に Cu 酸度 7 9 g/4, H<sub>2</sub>SO<sub>4</sub> 3 2 g/4, H<sub>2</sub>MoO<sub>4</sub> 0.4 g/4, H<sub>2</sub>SiO<sub>3</sub> 0.2 g/4 からなる电解液（液温 1 5 ℃）中にかいて 3 2 秒間、電流密度 4 A/cm<sup>2</sup> にて 2 次凹凸化鋼メッシュを行つて鋼層厚 1 8 μ の初期鋼層を得た。

#### 比較例 1

3 0 μ の脱酸アルミニウム合金箔（AL 99.7 %, Cu 0.5 %, P 0.0 5 %, Si 0.2 0 %）をアルソード 3 0 g/4, リン酸ソード 5 0 g/4 からなる电解液（液温 7 0 ℃）中に 3 分間浸漬して脱脂を行い、次いで脱アルミニウム合金箔の片面銀層 1 5 μ を選択的鍍 Zn 0.7 0 g/4, NaOH 4 0 0 g/4 からなる电解液（液温 3 0 ℃）中に 2 0 秒間浸漬して正味脱酸メッシュを行ひ、次いで脱アルミニウム合金箔の片面の全层に Cu 酸度 1 0 0 g/4, ピロリン酸カリウム 2 0 0 g/4,

Na<sub>2</sub>AlO<sub>4</sub> 1 2 H<sub>2</sub>O 0.9 g/4 からなる电解液（液温 1 2 ℃）中にかいて 2 0 秒間、電流密度 6 A/cm<sup>2</sup> にて 2 次凹凸化鋼メッシュを行つて鋼層厚 7 μ の初期鋼層を得た。

#### 比較例 2

5 0 μ の脱酸アルミニウム合金箔（AL 99.3 %, Cu 0.0 4 %, P 0.0 7 %, Si 0.1 5 %, Zn 0.0 8 %, Mg 0.1 0 %, Ti 0.0 8 %）をオルトケイ酸ナトリウム 1 0 0 g/4, NaOH 3 0 g/4, ノーチン不界面活性剤 0.1 g/4 からなる电解液中にかいて 3 0 秒間脱酸 2 A/cm<sup>2</sup> により脱酸电解過程を行ひ、次いで脱アルミニウム合金箔の片面（銀幅巾 1 5 mm）のみを選択的鍍 Zn 0.7 0 g/4, NaOH 4 0 0 g/4 からなる电解液（液温 3 0 ℃）中に 2 0 秒間脱酸せしめて両分层銀電極メッシュを行つた後、次いで脱アルミニウム合金箔を Cu 酸度 1 0 0 g/4, ピロリン酸カリウム 2 5 0 g/4, NH 9.0 からなるメッシュ（液温 6 0 ℃）中にかいて 1 5 分間、電流密度 3 A/cm<sup>2</sup> にて鍍メッシュを行ひ、次いで脱鋼メッシュ用

NH 9.0 からなるメッシュ（液温 4 0 ℃）中に 1 5 分間、電流密度 3 A/cm<sup>2</sup> にて鍍メッシュを行ひ、次いで脱メッシュの上に Cu 酸度 5 0 g/4, H<sub>2</sub>SO<sub>4</sub> 3 0 g/4 からなるメッシュ（液温 6 5 ℃）中にかいて 7 5 秒間、電流密度 3 2 A/cm<sup>2</sup> にて凹凸化鋼メッシュを行ひ、最後に脱凹凸化鋼メッシュの上に Cu 酸度 7 9 g/4, H<sub>2</sub>SO<sub>4</sub> 3 2 g/4, H<sub>2</sub>MoO<sub>4</sub> 0.4 g/4, H<sub>2</sub>SiO<sub>3</sub> 0.2 g/4 からなる电解液（液温 1 5 ℃）中にかいて 3 2 秒間、電流密度 4 A/cm<sup>2</sup> にて 2 次凹凸化鋼メッシュを行つて钢層厚 5 μ の初期鋼層を得た。

#### 比較例 3

比較例 1 と同様のアルミニウム合金箔を使用し、比較例 1 と同様に脱酸処理を行つた後正味脱酸メッシュを行ひことなく、直ちに比較例 1 と同様の鋼メッシュを行ひ更に凹凸化鋼メッシュを行つて钢層厚 5 μ の初期鋼層を得た。

而して上記実験例 1～3 及び比較例 1～3 により得た脱酸竹橋鋼箔をグラフエレガシ音波装置の上に置かれ、加热温度 1 8 0 ℃、E

力 2.5 kN/cm<sup>2</sup>において 60 分間加圧して、厚さ 2 mm の被覆板とした後、アルミニウム箔の板全体と強接着剤を剥して鋼板接頭部とした後、鋼板の厚さを 1.5 mm にするため、更にビヨーリン脱脂ノックを行い、溶接により接着力並にピンホールを発生した。その結果図 1 図に示す通りである。

また、荷重力は 1.0 kN 中につき 90° 方向の引き裂き力によるものであり、ピンホールは場所に依りて下方から光をあて透かす穴の状態をカウントした。

特許第16433回

本発明は従来方法により得た接頭部に比して、ピンホールが著しく少く且つ荷重力に依りて発れたものを得る接頭部を効果を有する。

出願人代筆人 先端士 鈴江武雄

図 1 図

|       | ピンホール数<br>(個/cm <sup>2</sup> ) | 引 破 力<br>(kN/cm <sup>2</sup> ) | 鋼板の外観     |
|-------|--------------------------------|--------------------------------|-----------|
| 鋼板例 1 | 2 ~ 4                          | 1.6 ~ 1.7                      | 鏡面ピロード状凹凸 |
| 2     | 1 ~ 2                          | 2.0 ~ 2.4                      | /         |
| 3     | 0                              | 2.0 ~ 2.4                      | /         |
| 比較例 1 | 20 ~ 200                       | 1.5 ~ 1.7                      | ラング状凹凸    |
| 2     | 無 数                            | 1.4 ~ 1.6                      | /         |

上表より甲かの細く平滑な方法により得た結果

## 5. 添付資料の目録

|        |    |
|--------|----|
| ① 著者証  | 2通 |
| ② 連絡書  | 1通 |
| ③ 送付料金 | 2通 |
| ④ その他  | 1通 |

## 6. 本件以外の免責者、許可出個人および代理人

## (1) 免 責 者

日本東日光市南高町 500番地  
古河電工株式会社日光研究所内  
在 居 人

## (2) 審査出願人

東京都千代田区丸の内二丁目6番1号  
古河電工株式会社  
代表取締役 白 橋 重吉

## (3) 代 理 人

住所 東京都千代田区丸の内二丁目6番1号  
氏名 (5743) 会員 三木 汽 雄